Two level system in microcanonical ensemble and negative temperature –

Let us take N no. of particles distributed in two levels having energies 0 and ϵ, which are the ground state and excited state, respectively. Let us define an excitation number n_i such that – $n_i = 0 \rightarrow$ ground state (energy 0)

$n_i = 1 \rightarrow$ excited state (energy ϵ)

Then, we can calculate the total energy of the system which is, $E = \sum_{i=1}^{N} n_i \epsilon = N_1 \epsilon$ where, N_1 = no. of particles in the excited state.

Now, the probability of finding a certain microstate in such a system will be, $p = p(\{n_i\}) = \frac{1}{\Omega(N,E)}$, where $\Omega(N,E)$ is the total no. of microstates available to the system (N,E) and constitute the macrostate. This follows from the equal a priori probability that all the microstates are equally probable and hence the probability of a given microstate is just one over the total no. of microstates for a given macrostate.

Now, $\boxed{\Omega(N,E) = \frac{N!}{N_1!\,(N-N_1)!}}$ —(1), which gives the total no. of microstates for a given macrostate. If we consider, N, N_1 and $(N-N_1) \gg 1$, ie, very large, we can use the Stirling approximation – $N! \simeq \left(\frac{N}{e}\right)^N$, $N_1! \simeq \left(\frac{N_1}{e}\right)^{N_1}$ and $(N-N_1)! \simeq \left(\frac{N-N_1}{e}\right)^{N-N_1}$ and putting in (1),

$$\Omega(N_1, E) = \frac{N^N}{N_1^{N_1}\,(N-N_1)^{N-N_1}} \quad (\because \text{the exponentials cancel out})$$

Taking logarithm on both sides and noting that the entropy is related to Ω by the Boltzmann expression, $S = k_B \ln \Omega$, we write –

$$\frac{S}{k_B} = N \ln N - N_1 \ln N_1 - (N-N_1)\ln(N-N_1) \quad \text{—②}$$

$(\because$ from eqn. ①$)$.

The value of thermodynamic temperature –

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N = \left.\frac{\partial S}{\epsilon\,\partial N_1}\right|_N \quad (\because E = N_1\epsilon).$$

$$\therefore \text{from ②},\ \frac{1}{T} = \frac{k_B}{\epsilon}\left[-\cancel{N_1}\cdot\frac{1}{\cancel{N_1}} - \ln N_1 - \cancel{(N-N_1)}\cdot 1\cdot\frac{(-1)}{\cancel{(N-N_1)}} + \ln(N-N_1)\right]$$

$$= \frac{k_B}{\epsilon}\left[-\cancel{1} - \ln N_1 + \cancel{1} + \ln(N-N_1)\right]$$

$$\text{or,}\quad \boxed{\frac{1}{T} = \frac{k_B}{\epsilon}\ln\left(\frac{N-N_1}{N_1}\right)} \quad \text{—③}.$$

From the properties of logarithm, $\ln x > 0$ if $x > 1$; if $x < 1$ then $\ln x$ is –ve. So, in this case, from eqn. ③, for the log term to stay +ve, $\frac{N-N_1}{N_1}$ should be greater than 1, and then $T > 0$.

$$\text{ie,}\quad \frac{N-N_1}{N_1} > 1,\ \text{ie,}\ N-N_1 > N_1 \Rightarrow N > 2N_1 \text{ or, } N_1 < \frac{N}{2}.$$

This is the condition for $T > 0$. T turns out to be negative if the no. of particles in the excited state is more than half the total no. of particles in the system (ie, N). The population in the excited state can be increased by supplying energy to the system.

So, for this classical system, one cannot increase the population of the excited state by more than half of the total population. This becomes more clear if we look at the energy argument.

From eqn. ③, $\frac{\epsilon}{k_B T} = \ln\left(\frac{N-N_1}{N_1}\right)$.

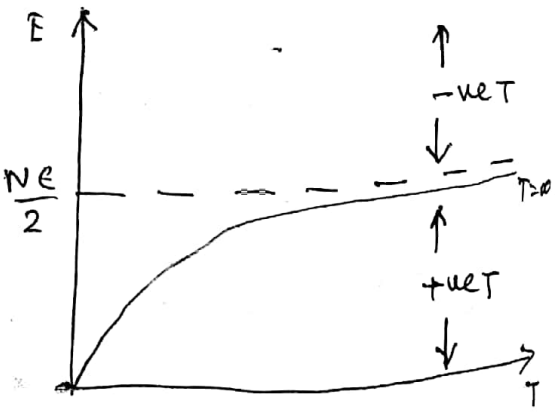
or, $\frac{N-N_1}{N_1} = e^{\epsilon/k_B T} \Rightarrow \frac{N}{N_1} = 1 + e^{\epsilon/k_B T} \Rightarrow N_1 = \frac{N}{1+e^{\epsilon/k_B T}}$

multiplying both sides by ϵ, $N_1\epsilon = \frac{N\epsilon}{1+e^{\epsilon/k_B T}}$.

or,
$$\boxed{E = \frac{N\epsilon}{1+e^{\epsilon/k_B T}}} \quad \text{---} ④$$

If we sketch the energy E vs. T; for $T \to \infty$, $e^{\epsilon/k_B T} \to 1$ and, we get the maximum energy $E = \frac{N\epsilon}{2}$. $(= N_1\epsilon$ where $N_1 = N/2)$

The region below the dashed line is the region of +ve temperature. Now, if we push the temperature to $T \to \infty$, we can get a population of $N_1 = \frac{N}{2}$. To put more particles in the excited state is thus impossible. Hypothetically, if we consider a system with $N_1 > \frac{N}{2}$, then the temperature of the system has to be -ve, but this -ve temperature has to be hotter than infinite temperature, which is apparently contradictory from the classical point of view. So, one cannot go on heating the system to attain -ve temper-ature.



However within the ambit of statistical interpretation, a state of negative temperature is possible. As an example is a system of independent, non interacting spins of spin $\frac{1}{2}$ separated from one another on a lattice in a magnetic field H. The spins aligned with the field have a lower energy than those aligned against the field. Then, $\epsilon\uparrow = \epsilon_0$ and $\epsilon\downarrow = \epsilon_1$ and the separation between the energy levels is $\Delta\epsilon = 2\mu H$. Such a system of free spins is called an ideal paramagnet. For independent spins, the occupation of the $\epsilon_1 = \Delta\epsilon$ and $\epsilon_0 = 0$ states (say) is given by the Boltzmann factor –

$$N_1 = \frac{e^{-\Delta\epsilon/k_BT}}{1 + e^{-\Delta\epsilon/k_BT}}, \quad N_0 = \frac{1}{1 + e^{-\Delta\epsilon/k_BT}} \qquad \text{—— (1)}$$

and $$\frac{N_1}{N_0} = e^{-\Delta\epsilon/k_BT} \qquad \text{—— (2)}.$$

Eqn. (2) shows that at $T \to 0$ all spins will be in the lowest energy state ϵ_0 and the spin system will be fully aligned in the field ($N_1 = 0$). At $T \to \infty$ there is an equal occupation of ϵ_1 and ϵ_0 ($N_1 = N_0$) and zero net magnetization. As noted the spins are either electron spins or nuclear spins and the remainder of the solids is referred to as lattice. At equilibrium the temperature of the spins ($\beta = \frac{1}{k_BT}$ ie, $T = \frac{1}{k_B\beta}$) is the same as that of the rest of the lattice and this temperature sets the magnetization in the spin system. However, the thermal contact between the spin system and the lattice can often be very poor so that a distinct spin temperature T_s becomes possible. This spin temperature is defined by eqn. (2) by the ratio of N_1/N_0. To see how T_s can take a -ve value suppose a field H is applied so that N_1/N_0 is given by eqn. (2). We now

reverse the direction of H so that $\epsilon_0 > \epsilon_1$. The spin system takes a finite time to 'relax' to the appropiate population of N_1 and N_0 and immediately after the switch we have - $N_0/N_1 = e^{\Delta\epsilon/k_BT}$ —③. The spin temperature is then said to be negative. Eventually as the spins 'relax' the spin temperature goes over to that of the lattice and becomes +ve again. The initial -ve temperature is defined only in a statistical sense via eqn. ③ and could not be reached by a slow thermodynamic process from one equilibrium state to another. Simply, a -ve temperature means that higher energy levels have higher occupation than the lower energy levels so that the sign is reversed in the Boltzmann factor.

Negative temperature is fundamental to LASER operation. Suppose ϵ_0 and ϵ_1 are electron energy levels. we can simulate transition between the two levels by shining light of frequency $h\nu_0 = \Delta\epsilon = \epsilon_1 - \epsilon_0$ on the system. Since the transition probability for absorption and emission of photons is equal the populations N_1 and N_0 becomes equal for intense light ($T = \infty$). Suppose now that by another process, we can continually over populate level ϵ_1 so that $N_1 > N_0$ ($T < 0$). This can be done by pumping electrons from level ϵ_0 to suitable higher energy states which decay to ϵ_1. This pumping can be acheived using a second light beam of a higher frequency and is called optical pumping. If we now pass the original beam of frequency ν_0 through this system, having $N_1 > N_0$ it stimulates transitions from ϵ_1 to ϵ_0 and a net emission of photons having identical frequency ν_0 results. The original beam is then

amplified and we get light amplification by similated emission of radiation (photons). This amplification depends entirely on the two level system having a negative temperature.

Classical theory of radiation

Properties of thermal radiation — According to Maxwell, thermal radiation is defined as the transfer of heat from a hot body to a cooler body without appreciable heating of the intervening medium (or space). Heat or thermal energy is propagated by radiation, just like the light energy propagates, it being an electromagnetic wave. The thermal radiation has the following properties —

1. Thermal radiation has electromagnetic wave nature and hence travel through empty space (no material medium is necessary) with the velocity of light.
2. Like light, thermal radiation travels in straight line.
3. Thermal radiation obeys the law of inverse square.
4. It exhibits reflection, refraction, interference, diffraction and polarization phenomenon.
5. Thermal radiation is frequently called as infrared radiation.

Black body radiation —

A perfectly black body is one which absorbs totally all the radiation of any wavelength which falls on it. As it neither reflects nor transmits any radiation, it appear black, whatever be the colour of

radiation. The main characteristics of such a body is that when heated to a suitable high temperature, it emits full or total radiation. As it is a perfect absorber, it is also a perfect radiator, its emission being the greatest possible for every wavelength at any given temperature.

When a black body is placed inside a uniform temperature (isothermal) enclosure, it will emit full radiation of the enclosure after it is in equilibrium with the enclosure. These radiations are independent of the nature of the substance, nature of walls of the enclosure, and presence of any other body in the enclosure but depends only on temperature. Since a perfectly black body is one which absorbs all the radiation that falls on it, of whatever wavelength they may be, the radiation emitted by it will possess a character independent of the property of any particular substance, purely dependent on the temperature to which it is raised. Hence it is solely temperature dependent. Such radiation in a uniform temperature enclosure are known as black body radiation.

Kirchoff's law —

kirchoff's law states that the ratio of the emissive power to the absorptive power for a given wavelength at a given temperature is the same for all bodies and is equal to the emissive power of a perfectly black body at that temperature.

Suppose a_λ is the absorptive power of a body. Let dQ be the quantity of heat energy lying within the wavelength λ and $\lambda + d\lambda$,

incident on unit area of the surface per second, then the quantity of heat energy absorbed by the surface is given by $a_\lambda d\varphi$. The remaining energy $(d\varphi - a_\lambda d\varphi) = d\varphi(1-a_\lambda)$ will be either reflected or transmitted or both. If e_λ is the emissive power, then, the amount of energy emitted per unit time per unit area between wavelengths λ and $\lambda + d\lambda$ by virtue of the temperature, is given by $e_\lambda d\lambda$. Thus the total energy given out per unit time per unit area of the surface will be $= (1-a_\lambda) d\varphi + e_\lambda d\varphi\lambda$.

In equilibrium state, $d\varphi = (1-a_\lambda) d\varphi + e_\lambda d\lambda$

or, $a_\lambda d\varphi = e_\lambda d\lambda$. —①

For a perfectly black body, $a_\lambda = 1$ and $e_\lambda = E_\lambda$, where E_λ is the emission power of a perfectly black body.

$\therefore d\varphi = E_\lambda d\lambda$ —②.

Substituting in ①, we get — $a_\lambda E_\lambda d\lambda = e_\lambda d\lambda$.

or, $\boxed{E_\lambda = \frac{e_\lambda}{a_\lambda}}$ —③

This is known as Kirchoff's law.

Kirchoff's law tell us that good absorbers are good emitters. If a body absorbs radiation of a particular wavelength strongly, it also emits the same radiation strongly. A sodium vapour which emits two yellow lines (D_1 and D_2 of wavelengths 5890 Å and 5896 Å) strongly is also a good absorber of light of these two wavelengths. The origin of

Fraunhofer dark line in sun's spectrum is successfully explained. When the radiation from the central glowing mass which gives continuous spectrum passes through the surrounding atmosphere containing various elements like hydrogen, nitrogen, sodium, cesium, copper etc., in the gaseous state, absorb those wavelengths which they can emit at a higher temperature. As a result, those wavelengths are missing from the sun's spectrum and dark lines are seen in their place. The nature and origin of characteristics spectra of elements is also successfully explained by the kirchoff's law.

Stefan - Boltzmann law —

Stefan's law: It states that the rate of emission of radiant energy per unit area of a perfectly black body is directly proportional to the fourth power of its absolute temperature.

ie, $E = \sigma T^4$ —(1)

where σ is a constant called Stefan's constant. The value of σ is 5.67×10^{-8} W $m^{-2} K^{-4}$.

Stefan's law refers to the emission of heat radiation only by the body itself, and not to the net loss of heat by the body after exchange with the surroundings. It simply deals with the amount of heat emitted by the body by virtue of its temperature irrespective of what it receives from the surroundings. The law can be extended to represent the net loss of heat and may be enunciated as follows:

If a black body at absolute temperature T is surrounded by another black body at absolute temperature T_0, the net rate

of loss of heat energy per unit area of the surface is given by -

$$E \propto (T^4 - T_0^4)$$

or, $$E = \sigma (T^4 - T_0^4) \quad \text{—②}$$

This is in accordance with the Prevost's theory of heat exchange, i.e, the net loss of heat is really the difference in the heat radiated by the hot body and that absorbed by it from its surroundings. This law given by eqn. ② is known as Stefan–Boltzmann law.

If a body has emissivity of e, then total energy radiated by the body per unit time is $= e\sigma (T^4 - T_0^4)$ —③.

Thermodynamical proof –

The black body radiation exerts pressure similar to a gas. Hence thermodynamical relations are applicable to heat radiation. Let u be the energy density of radiation inside an uniform temperature enclosure at temperature T. Suppose P is the pressure and V, the volume of the enclosure.

From 1st law of thermodynamics, $dQ = dU + PdV$.

Applying the second thermodynamical relation $\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$

$$\left(\frac{\partial U + P\partial V}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad \text{—①}$$

Since V is the volume of the enclosure, then the total internal energy of radiation in the enclosure is given by, $U = uV$ —(2)

and the pressure exerted $P = \frac{u}{3}$ — (3).

Now, differentiating (2) w.r.t. V, keeping T constant, we get

$$\left(\frac{\partial U}{\partial V}\right)_T = u.$$ Here $u = u(T)$ fn. of temperature alone.

Substituting in (1), $u = \frac{T}{3}\frac{du}{dT} - \frac{u}{3}$.

or, $\frac{4}{3}u = \frac{T}{3}\frac{du}{dT}$

or, $\frac{du}{u} = 4\frac{dT}{T}$

integrating, $\log u = 4 \log T + \text{constant}$

$= 4 \log T + \log A$ —(4)

where $\log A$ = constant of integration.

or, $\boxed{u = AT^4}$ —(5)

Also the total rate of emission per unit area of a black body is proportional to the energy density.

$\therefore E \propto u$

or, $E \propto T^4$

or, $\boxed{E = \sigma T^4}$ —(6)

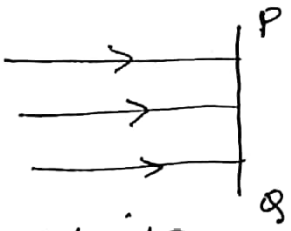
where σ is the Stefan's constant.

Radiation pressure –

1. Normal incidence – The radiation possesses the properties of light. As we know, light exerts a small but definite pressure on the surface on which it is incident. Maxwell proved on the basis of his e.m. theory that the pressure is equal to the energy density (i.e, the amount of radiation per unit volume) for normal incidence on a surface. The expression for the pressure of radiation is derived on the basis of quantum theory. Consider a photon of energy $h\nu$ moving with speed c (i.e, the speed of light). According to the theory of relativity, this energy of the photon corresponds to a mass m given by –

$$mc^2 = h\nu$$

$$\text{or, } m = \frac{h\nu}{c^2}$$



Then the momentum of the photon = mass × velocity

$$= \frac{h\nu}{c^2} \times c = \frac{h\nu}{c}$$

$$= \frac{e}{c}$$

where $e = h\nu$ is the energy of the photon.

Now momentum incident on the surface per unit area per unit time is given by – $P = \sum \frac{e}{c} = \frac{\Sigma e}{c}$ —(1).

But, Σe = total energy incident on the surface per unit area per unit time = E (say). Putting in (1), $P = \frac{E}{c}$. —(2).

If 'u' is the energy density, i.e, energy per unit volume, then the total

energy passing through an area 's' of the surface normal to the incident radiation per unit time = ucs.

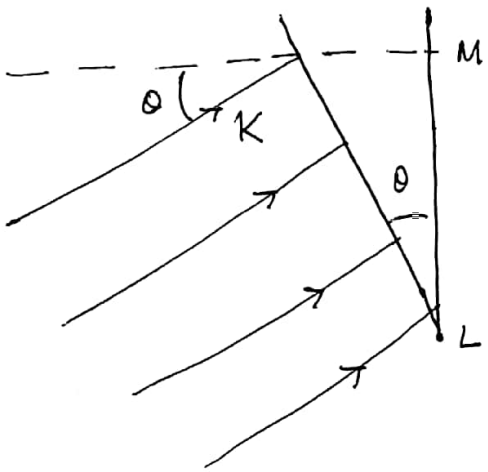
∴ The energy flux, ie, energy radiation per unit area per unit time is, $E = \frac{ucs}{s} = uc$. Substituting in (2), $P = \frac{uc}{c} = u$.

$$\therefore \boxed{P = u} \quad \text{——— (3)}$$

If all of this momentum is absorbed, it will give rate of change of momentum per unit area, ie, the pressure of radiation $P = u$. Thus for normal incidence on the surface, the pressure of radiation is equal to the energy density.

Pressure of diffused radiation —

Suppose the radiation is diffused, ie, the photons move in all possible directions. Let the incident beam of radiation make an angle θ with the normal to the surface LM. The energy incident on the surface KL per unit area per unit time = uc.



If s is the surface area of plane KL, the energy incident on the surface KL per unit time = uc.s.

But, the surface area of the plane KL = surface area of plane LM × cosθ

$= s'\cos\theta$.

where s' = surface area of plane LM.

∴ Energy incident on the surface KL per unit time $= uc s' \cos\theta$.

From the figure, it is obvious that the total energy crossing the plane LM / unit time is equal to the energy incident on the plane LM per unit time.

∴ Energy incident on LM / unit time $= uc s' \cos\theta$.

∴ Energy per unit area per unit time $= \dfrac{uc s' \cos\theta}{\text{surface area of LM}}$.

$= \dfrac{uc s' \cos\theta}{s'} = uc\cos\theta$. —④

∴ the momentum incident on the surface LM per unit area per unit time $= \dfrac{uc\cos\theta}{c} = u\cos\theta$.

The component of this momentum in a direction normal to the surface LM $= u\cos\theta \cdot \cos\theta = u\cos^2\theta$. —⑤

If all this momentum is absorbed, then equation ⑤ gives the total rate of change of momentum per unit area normal to LM, i.e, the pressure of radiation on the surface LM is given by — $u\cos^2\theta$. —⑥.

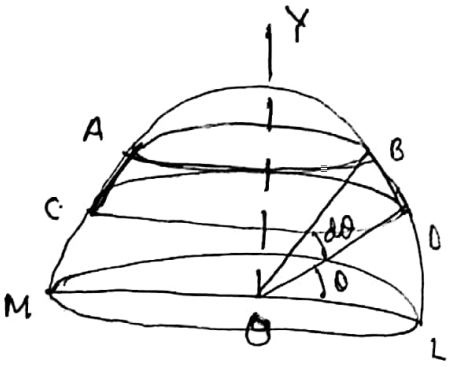
In the case of diffused radiations, the radiation is incident from all possible directions with equal probability. Therefore, if there are N beams of radiation meeting the surface, the total radiation pressure on the surface is given by — $\Sigma u\cos^2\theta$. —⑦.

In order to calculate $\Sigma u\cos^2\theta$, imagine a hemisphere of radius r, around the centre O of the element LM.

Now from the surface of the hemisphere cut out a ring shaped

element ABCD by means of two cones of angles θ and $\theta + d\theta$ drawn from O as apex and OY (which is ⊥r to LM) as axis.

The area of the ring $= 2\pi r^2 \sin\theta \, d\theta$.



As N beams are considered to be uniformly distributed over the surface of the hemisphere which is equal to $\frac{1}{2} \times 4\pi r^2 = 2\pi r^2$. The number of beams crossing through the area of the ring $-$

$$dN = \frac{2\pi r^2 \sin\theta \, d\theta}{2\pi r^2} \cdot N = N \sin\theta \, d\theta. \quad \text{—(8)}$$

Fraction of beams incident between angle θ and $\theta + d\theta = \frac{dN}{N}$

$$= \sin\theta \, d\theta.$$

The pressure p can then be written as $p = \frac{dN}{N} \cdot u \cos^2\theta$

$$= \sin\theta \, d\theta \cdot u \cos^2\theta.$$

$$= u \sin\theta \cos^2\theta \cdot d\theta.$$

$$\therefore \quad p = \int_0^{\pi/2} u \sin\theta \cos^2\theta \, d\theta$$

$$= u \int_0^{\pi/2} \cos^2\theta \cdot \sin\theta \, d\theta.$$

$$= u \cdot \frac{1}{3}$$

$$\therefore \quad \boxed{p = \frac{u}{3}}.$$

∴ Pressure of diffused radiation, $p = \frac{1}{3} \times$ total energy density.

Wein's displacement law + Wein's distribution law —

From thermodynamic considerations, Wein showed that the product of the wavelength corresponding to the maximum energy (E_{max}) (with corresponding wavelength λ_m) and the absolute temperature T is constant, ie,

$$\boxed{\lambda_m T = \text{constant}} \quad \text{—— (1)}.$$

This is Wein's displacement law. The value of the constant is 0.2892 cm.K. This law shows that as the temperature is raised, the maximum intensity of emission is displaced towards the shorter wavelength side. This is why it is called Wein's displacement law.

Wein also showed that the energy E_{max} is directly proportional to the fifth power of the absolute temperature, $E_{max} \propto T^5$.

ie, $E_{max} \cdot T^{-5} = \text{const.}$ —— (2).

$\therefore \quad E_\lambda = c\lambda^{-5} f(\lambda T)$ —— (3).

where E_λ is the emissive power of the black body which has a maximum value at the absolute temperature T. Here c is a constant and $f(\lambda T)$ is some function of λT.

To determine the form of $f(\lambda T)$, Wein made some arbitrary but plausible assumptions concerning the actual mechanism of emission and absorption of radiation and concluded that the function should have the form $Ae^{-a/\lambda T}$

$$\therefore \quad E_\lambda = c\lambda^{-5} A e^{-a/\lambda T}.$$

$$= K\lambda^{-5} e^{-a/\lambda T}.$$

where K is another constant having value 4.94×10^{15} C.G.S. units and another constant 'a' has value 1.43 cm-degree. Multiplying both sides by $d\lambda$, we have — $E_\lambda d\lambda = K\lambda^{-5} e^{-a/\lambda T} d\lambda$

Now, $E_\lambda d\lambda$ represents the amount of energy dE associated with the spectral region lying in the wavelength range λ and $\lambda + d\lambda$ emitted by a black body at a temperature T

$$dE = K\lambda^{-5} e^{-a/\lambda T} d\lambda$$

This expression is known as <u>wein's law of energy distribution.</u>

The success of wein's law is that it holds good in the region of shorter wavelengths at lower temperatures. It doesnot hold good at longer wavelengths at higher temperatures.

<u>Raleigh Jean formula and ultraviolet catastrophe —</u>

Lord Raleigh and James Jean studied the nature of blackbody radiation. In their study, they started by considering the radiation inside a cavity at absolute temperature T whose walls are perfect reflectors as — a series of standing e.m. waves. The number of independent standing waves $G(\nu)d\nu$ in the frequency interval ν and $\nu + d\nu$ per unit volume, $G(\nu)\,d\nu = \dfrac{8\pi\nu^2 d\nu}{c^3}$

This formula is independent of cavity shape. Now, to find the average energy per standing wave, we can consider each standing wave originating from the oscillation of electric charge inside the cavity wall. Now an one dimensional oscillator has two degrees of

freedom, one corresponding to its kinetic energy and one corresponding to its potential energy. Hence two degrees of freedom are associated with the standing waves, and, it should have an average energy of $2 \times \frac{1}{2} kT$, ie, $\bar{\epsilon} = kT$. The $\frac{1}{2} kT$ originating from the law of equi-partition of energy. The total energy $u(\nu)\, d\nu$ per unit volume in the cavity in the frequency range ν and $\nu + d\nu$ is therefore,

$$u(\nu)\, d\nu = \bar{\epsilon}\, g(\nu)\, d\nu = \frac{8\pi kT}{c^3} \nu^2 d\nu \qquad \text{—①}$$

or in terms of λ, $\quad u(\lambda)\, d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda$.

This is the <u>Raleigh-Jean formula</u>.

From eqn. ① it is evident that as $\nu \to$ higher frequency, $u(\nu)$ should increase as ν^2. So, as $\nu \to \infty$, $u(\nu) \to \infty$. However, in reality, the energy density (and radiation rate) falls to zero as $\nu \to \infty$. This discrepancy is called the <u>ultra violet catastrophe</u>.

<u>Saha ionization equation</u> —

The saha ionization equation gives the relative number of atoms in two ionization states as a function of electron density n_e and temperature T.

$$\frac{n_{r+1}\, n_e}{n_r} = \frac{g_{r+1} g_e}{g_r} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \exp\left(\frac{-\chi_r}{k_B T} \right)$$

Here n_r and n_{r+1} are the no. densities of atoms in the ionization state r and the ionization state $r+1$ of a given element. Also, n_e is the electron number density, G_r and G_{r+1} are the partition functions of the two states, $g_e = 2$ is the statistical weightage of electron, m_e is the electron mass, and χ_r is the ionization potential from state r and $r+1$.

The equation is a result of combining ideas of quantum mechanics and statistical mechanics and is used to explain the spectral classification of stars. This expression was developed by Meghnad Saha in 1920 in Calcutta.

Radiation pressure using B-E statistics and partition function –

Consider an enclosure containing electromagnetic radiation. If the enclosure is maintained at a temperature T, it will emit and reabsorb photons. After a certain time has lapsed, a situation will be established in which the photons and the walls of which the cavity is composed, will be in thermodynamic equilibrium. The number of photons in such an enclosure is not definite; but its total energy remains constant. The electromagnetic radiation within the enclosure is called black body radiation.

Such a radiation may be considered as a gas of photons. The state of a photon can be specified by the magnitude and direction of its momentum and by the direction of polarization

of the e.m. waves associated with it. If the wave is regarded as quantized, then the photon is considered as a relativistic particle of energy $\epsilon = \hbar\omega$ and momentum $|\vec{p}| = \frac{\hbar\omega}{c}$. The photons have integral spin and, hence, the photon gas obeys Bose statistics.

Since the gas is in equilibrium, its free energy must be minimum, ie, $\frac{\partial F}{\partial N} = 0$.

∴ The chemical potential of the photon gas, $\mu = 0$.

The grand partition function Z, therefore is given by –

$$Z = \sum e^{-\beta n_i \epsilon_i} = \prod_i \left[1 - e^{-\beta\epsilon_i}\right]^{-1} \quad \text{—①}.$$

$$\therefore \ln Z = -\sum_i \ln\left[1 - e^{-\beta\epsilon_i}\right]$$

$$= -\sum_i \ln\left[1 - e^{-\beta h\nu_i}\right] \quad \text{—②}.$$

The number of allowed states with momentum between p and $p+dp$ is $(4\pi V/h^3)\, p^2 dp$. or in terms of frequency, the number is

$$\frac{4\pi V}{h^3} \cdot \frac{h^2\nu^2}{c^2} \cdot \frac{h}{c} \cdot d\nu = \frac{4\pi V}{c^3}\nu^2 d\nu \quad \text{—③}.$$

However, in the photon gas, there are two independent directions of polarization of the electromagnetic wave, perpendicular to its direction of propagation. Each photon may have one of these directions of polarization, and, hence, the number of allowed states is doubled, ie, it is equal to $\frac{8\pi V}{c^3}\nu^2 d\nu$

$\therefore$ The number of allowed states per unit volume $= \frac{8\pi}{c^3}\nu^2 d\nu$.

Replacing the summation by integration,

$$\ln Z = -\frac{8\pi V}{c^3}\int_0^\infty \nu^2 \ln\left[1 - e^{-h\nu/kT}\right] d\nu \quad \text{—(5)}.$$

Integrating by parts, $\ln Z = \left[-\frac{8\pi V}{c^3}\cdot\frac{\nu^3}{3}\cdot\ln\left(1-e^{-h\nu/kT}\right)\right]_0^\infty$

$$+ \frac{8\pi V}{3c^3}\int_0^\infty \frac{\nu^3 e^{-h\nu/kT}}{1-e^{-h\nu/kT}}\cdot\frac{h}{kT}\cdot d\nu,$$

The 1st integral vanishes at both the limits.

$$\therefore \ln Z = \frac{8\pi V h}{3c^3 kT}\cdot\int_0^\infty \frac{\nu^3 d\nu}{e^{h\nu/kT}-1} \quad \text{—(6)}.$$

Substituting $x = \frac{h\nu}{kT}$, $\ln Z = \frac{8\pi V h}{3c^3 kT}\left(\frac{kT}{h}\right)^4\int_0^\infty \frac{x^3}{e^x-1}dx$

$$\text{or, } \ln Z = \frac{8\pi V}{3}\left(\frac{kT}{hc}\right)^3\frac{\pi^4}{15}$$

$$= \frac{8\pi^5 V}{45}\left(\frac{kT}{hc}\right)^3. \quad \text{—(7)}.$$

Now, $\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = +kT^2\frac{\partial \ln Z}{\partial T}$

$$= \frac{8\pi^5 V}{45}kT^2\cdot\frac{3(kT)^2 k}{h^3c^3} = \frac{8\pi^5 V}{15c^3h^3}\cdot(kT)^4 \quad \text{—(8)}.$$

and, $\bar{P} = \frac{1}{\beta}\cdot\frac{\partial \ln Z}{\partial V} = \frac{8\pi^5}{45}\frac{(kT)^4}{h^3c^3}$

$$\therefore \quad \bar{P}\bar{V} = \frac{1}{3}\bar{E} \quad , \text{ ie, } \quad \bar{P} = \frac{1}{3}\frac{\bar{E}}{V} \, .$$

Thus, the pressure of radiation is equal to one third of the energy density, a well known result of the radiation theory.